THE INCLUSION AND OCCLUSION OF SOLVENT IN CRYSTALS.

An Insidious Source of Error in Quantitative Chemical Investigation.

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Perhaps the most frequent and the most insidious cause of error in quantitative chemical research is the unsuspected presence of water. The disturbing effect of this impurity is frequent, because water is one of the most plentiful of substances; and insidious, because there is usually no easy quantitative or qualitative test for small quantities of it.

The object of this paper is to recount several experiments indicating the prevalence and magnitude of inaccuracy from this cause, to show how many published results have been vitiated by it, to emphasize the theoretical aspect of the phenomenon, and especially to point out the methods of reducing the inaccuracy to a minimum.

In a number of isolated cases it has been shown by various chemists that substances crystallizing from a solution enclose within their crystals small quantities of the mother-liquor. It is very well known, for example, that crystals of common salt explode or decrepitate upon being heated, because of the vaporization of the enclosed water. Thus when common salt is weighed some water is weighed with it. This water is not combined as water of crystallization, of which common salt has none; it is entirely accidental. Following the nomenclature of the mineralogists, a liquid imprisoned in this way is best called "Included solvent." The mother-liquor is thus imprisoned, in addition to combined water, also in salts which contain this latter as an essential part of their crystal structure; in these cases it is even more difficult to detect and more generally overlooked, because of the simultaneous presence of the combined water.

Although these facts have been thus occasionally pointed out, the frequency of the occurrence of this cause of error has not often been realized by quantitative analysts. It is no careless exaggeration to state that in all my chemical experience I have never yet obtained crystals from any kind of solution entirely free from accidentally included mother-liquor; and, moreover, I have never found reason to believe that anyone else ever has. Whether the

solvent is water, an organic liquid, or a fused salt at high temperature, and whether the crystallization is quick or slow, in small or large crystals, the effect is always traceable, although of course in varying degrees. The amount of the enclosure varies from perhaps 0.01 per cent. to 0.5 per cent. of the total weight of the crystals.[1]

As a general rule, the clearer the crystal, the less the included mother-liquor; but appearance is not a wholly safe guide, since sometimes the refractive index of the mother-liquor is not far from that of the crystal. In this case the included impurity is invisible. Moreover, the inclusion may, and undoubtedly does, often occur in cells so small as to be beyond the reach of the best microscope.

It is not contended that the production of a perfectly pure crystal from a solution is impossible, but only that no evidence has been obtained proving that this end has ever artificially been reached, while much contrary evidence is available.

In looking over the records of the determinations of atomic weights, it is surprising to see how many experimenters in even this most exact field of quantitative analysis have either entirely overlooked the danger, or have taken inadequate means to overcome it. This is especially true when the salts to be weighed contain combined water of crystallization; indeed it is almost safe to rule out utterly all such results, without further consideration. Among other more or less vitiated cases, where salts supposedly anhydrous have been weighed, may be mentioned especially a number of the analyses of typical salts of osmium, iridium, platinum, and palladium. Often a painstaking but unthinking chemist has spent months in eliminating the *hundredth* of a per cent. of some foreign metal and finally ignored the *tenth* of a per cent. of water in his preparation. It is not, however, the purpose of this paper so much to seek the errors in individual instances of past work, as to point out the ways in which these errors may be avoided in the future.

How then is this included solvent to be eliminated without decomposing the substance which we desire to weigh?

It is usually considered as a sufficient precaution to powder the material finely and expose it to the air for a short time, in order to allow the undesirable water to evaporate. This crude proceeding involves a double uncertainty; in the first place, the unwar-

[1] For examples of carefully obtained evidence, see Richards, *Proc. Amer. Acad. Arts and Sciences*, 23, p. 177 (1887); 26, p. 267 (1891); 28, p. 11 (1893); 29, p. 60 (1893); 33, p. 299 (1898); 35, p. 139 (1899); 37, p. 434 (1902); 38, p. 411 (1902).

ranted assumption is made that every hidden cell containing the mother-liquor has been split open by the pestle, and in the next place the equally unwarranted assumption is made that all the mother-liquor thus exposed evaporates into the uncertain mixture constituting the atmosphere of the laboratory.

The former of these assumptions will be considered first. Is it possible to open all the cells enclosing mother-liquor by means of any finite amount of powdering?

This question cannot be answered *a priori;* accurate experiments are needed to decide it, and no published work known to me seems to furnish the needed data. Accordingly a series of experiments was planned which involved the progressive powdering of a typical substance. In order to separate the powders of different degrees of fineness four pieces of brass netting were used, having openings about 0.5, 0.3, 0.23, and 0.16 mm. in diameter respectively. This netting was cleaned with acid and ammonia, and showed a brilliantly clean surface in the microscope.[1]

The test substance chosen was baric chloride, because careful experiments on the atomic weight of barium had shown that it may be analyzed with ease and accuracy. A pure finely-crystallized specimen of the salt was slowly and carefully powdered and sifted through the successive sieves. That which went through the finest sieve was still more finely powdered, until the average diameter of the particles as estimated in the microscope was perhaps one-twentieth of a millimeter, some being coarser and some finer. Each specimen was thoroughly air-dried.

Thus were obtained four examples of baric chloride containing crystal-water, of four different degrees of fineness, the coarsest particles averaging about a thousand times the bulk of the finest. Upon analysis by heating to constant weight at 400° these samples yielded respectively 14.780, 14.771, 14.763, and 14.760 per cent. of water.

The data, reduced to the vacuum standard, were as follows. The experiments were made in 1893:

No.	*Average diameter of particles.*	*Weight of salt.*	*Loss on heating.*	*Per cent. of water found.*
1	0.45 mm.	4.15929	0.61475	14.780
2	0.27 mm.	3.65127	0.53933	14.771
3	0.20 mm.	4.54136	0.67047	14.763
4	0.05 mm.	10.13720	1.49620	14.760

[1] The material sifted through this netting was tested for copper, with satisfactorily negative results.

The results thus show a steady decrease in the amount of water as the powder becomes finer; hence each successive powdering must have opened new cells.

When the figures are plotted a somewhat irregular curve is obtained, the study of which seems to show that further powdering would have but little effect upon the last-named amount of water held by the crystals. As a matter of fact, among many scores of determinations of the quantity I have never found in a pure specimen of baric chloride less water than this. Is this limit then, observed in the very fine state of division, the true amount of water in the salt? This question is easily answered in the negative, for from the universally accepted atomic weights of barium, chlorine, oxygen and hydrogen it is easy to calculate that the theoretical amount of water is 14.744 per cent., an amount less by one part in a thousand than the lowest limit recorded above.

Similar results were obtained from cupric sulphate, and it seems probable that any other salt would behave in the same way. Thus it appears that although powdering and drying will diminish the excess of solvent, it will not wholly remedy the error. It is probable that anything short of molecular division would fail to open the minutest enclosing cells, although the larger cells are broken up with comparative ease.

The irregular shape of the curve drawn from the data given suggests that there is another cause of error superposed upon the effect just studied—an influence which grows in magnitude as the fineness of the powder is increased. A moment's reflection serves to show what this new cause of error must be.

It is well known that water adheres to or wets almost anything, except a few fats and oils; and even these absorb or dissolve water to some extent. In consequence of this tendency to adhere, water is condensed or *adsorbed* in an invisible film, from the always slightly moist atmosphere, upon the exposed surface of nearly all substances. This adhering film increases the weight of these substances.

The extent of the adsorption varies with the nature of the substance and in many cases is easily appreciable. With a given substance it is of course dependent upon the pressure of the aqueous vapor and the temperature, as well as upon the extent of surface.

Since the adsorption increases with the surface it is evident that fine pulverization, while tending to diminish the inclusion, will

tend to increase this new cause of error by increasing the field of its action.

Thus the irregularity of curve shown by the results with baric chloride is easily explained, as well as the abiding presence of an excess of water. In the effort to escape the Scylla of inclusion the chemist has run foul of the Charybdis of adsorption.

Adsorption of aqueous vapor can be eliminated by greatly raising the temperature or by greatly reducing the tension of the surrounding aqueous vapor. These means may be used either with anhydrous salts or with the sundry chemical vessels used for containing substances while weighing; but unfortunately either of these changes drives out also the crystal-water contained in a hydrated salt.

For these reasons it seems to me impossible to determine with the exactness demanded in the most accurate work the true weight of any salt containing water of crystallization.

In the case of *anhydrous* salts, which may be heated and placed in a perfectly dry atmosphere without decomposition, it is easy to eliminate adsorbed moisture, as already stated. It is not by any means so easy, however, to drive off the included solvent imprisoned in hidden cells. Some means must be used which disintegrates the walls of these cells; and the means adopted depends upon the nature of the substance being studied.

Either mechanical, thermal or chemical influences may be used to effect the disintegration. The mechanical means, pulverization, need not be further discussed. The application of heat first tends to vaporize the imprisoned solvent, if it is volatile, causing great pressure in the small space. This pressure often causes the enclosing cell to explode, and thus the solvent is set free. It is not by any means certain, however, that all the cells are thus able to discharge their contents, especially in tenacious substances; and in many cases hours of intense heating are necessary to drive off every trace of water, as with silica and iron rust. In the case of metals precipitated as such from aqueous solutions, temperatures not far from the melting-points must be used for drying, in order that their condition may be soft enough to yield to the internal pressure of the enclosed solvent. This precaution has usually been overlooked by physicists determining electro-chemical equivalents, although Lord Rayleigh pointed it out in the special case of silver twenty years ago.

A much safer plan, where it is practicable, is to *fuse* the cystalline precipitate. With the freedom of motion given by the liquid state volatile impurities usually soon escape, leaving the fused mass free from them. It is true that there is often danger that a portion of the substance itself will evaporate, or at least that it will attack the containing vessel; minute precautions must be used to avoid these causes of error. In extreme exigency the electrolysis of the fused mass, a plan suggested by Richard Lorenz, may be used as a means of destroying the last traces of water; but in most cases these may be swept out by the vapors from easily decomposed ammonium salts, just as bubbling air sweeps out carbonic acid from its solution.

A yet further and better thermal means of preparing a substance free from water is to vaporize and condense or sublime it in a perfectly dry atmosphere. Here crystals form under conditions excluding water, and the danger is wholly overcome. Unfortunately other impurities are usually introduced from the walls of the vessel used for the sublimation; but frequently these may be found by analysis much more directly and precisely than the water could be.

A chemical method of disintegrating the structure of a substance crystallized from a solution has been alluded to above. This method, although not always available, may sometimes serve when the other methods are inapplicable, and is often of great use in preparing chemically pure substances. This procedure, like the others, has been used in individual cases for years; but it does not seem to have been emphasized as a general method.

In brief the chemical method is as follows: The substance is crystallized from the solution, not directly in its desired form, but rather in chemical combination with a large quantity of some other substance which may be volatilized by suitable subsequent treatment. The clear, dry crystals are then subjected to this decomposing treatment, and the volatile constituent is expelled. The substance sought is thus left in the form of a porous mass, a skeleton of the former crystal, in which every cell enclosing mother-liquor has been opened by the chemical disintegration of its walls. From such a skeleton soluble impurities may often be washed out by lixiviation, and volatile ones escape at once.

For example, it is easier thoroughly to dry sodic carbonate when this salt is crystallized with its maximum amount of crystal-water,

than it is when the salt is crystallized immediately in the form devoid of crystal-water. Again, it is far easier to obtain pure iron by the reduction of the oxide in hydrogen than it is by electrolytic precipitation direct from a solution.

Yet another chemical method might sometimes be helpful, although inherently of a somewhat restricted usefulness. In a careful study of the behavior of gases included in oxides,[1] it was found that in these compounds oxygen could work its way out from a cell in which it exists under pressure, while nitrogen could not. It is possible that this fact is typical of a general principle; that any substance may escape from pressure when this substance forms one of the easily dissociated components of the containing walls, by a process of alternate dissociation and recombination of the materials constituting these walls. Thus certain hydrated salts, heated to a temperature of perhaps 120° in superheated steam at atmospheric pressure, might in time part with their enclosed water without losing their water of crystallization. This inference will be further tested in the near future.

In this connection, one other point must be strongly emphasized, because of its important bearing both upon chemical purification and upon dynamic geology. The microscopic cells in a crystal contain not only the solvent, but also all the other substances in the solution. They are miniature samples of the solution, not perhaps in strict quantitative measure, because of varying adsorption, but at least qualitatively.

Hence, if a chemically pure substance is desired, great pains must be taken to keep away from the solution anything which cannot be expelled or extracted from the disintegrated crystal, after the enclosures have been opened. For example, pure iron must be obtained by the reduction of oxide or hydroxide obtained from the nitrate, not from the sulphate. If the latter salt were used, the iron would probably contain sulphur. This practice of continually avoiding impurities obviates also the possible danger from "solid solution," as van't Hoff pertinently terms the *homogeneous* distribution of foreign matter in a solid. Solid solution, or *occlusion*, may be said to be the limiting case of *inclusion*. In this limiting case the enclosing cells are so small as to contain only single molecules. The distinction between occlusion and inclusion in solids is theoretically interesting, corresponding perhaps to the difference

[1] Richards, *Am. Chem. Jour.*, 20, p. 701 (1898).

between true solution and colloidal solution in liquids; but for present practical purposes this difference need not be further emphasized.

All these considerations have been carefully heeded in the recent determinations of atomic weights made in this laboratory.

Since the fundamental properties of material have probably not changed since the archæan times of mineral growth, natural crystals must have been subject to the same effects as those grown to-day, and all except those formed by sublimation must contain traces of the solutions from which they once separated. In some cases, of course, the very slow formation might reduce the inclusion to a very small amount. Those minerals coming from aqueous solutions would be supposed to contain accidentally enclosed water (often erroneously confounded with the true water of constitution), while those separating under fused or metamorphic conditions would contain non-volatile impurities taken from their immediate surroundings. Of these impurities the non-volatile ones must certainly remain; and many of the volatile ones may also, if closely enough imprisoned. As a matter of fact, we are very familiar with the traces of impurity in natural crystals, even the clearest of diamonds leaving some ash on combustion.

While the selective effects of adsorption and solid solution and the results of subsequent pressure must complicate the interpretation of these facts, and forbid their immediate quantitative utilization, it seems to me nevertheless that these enclosed traces of impurity might be used more often than they are used in geological reasoning, in order to discover the media from which crystals have separated, and hence the mechanism of their formation. Thus a phenomenon very troublesome to the chemist might become very useful to the geophysicist.

The contents of this paper may be summarized briefly as follows:

(*a*) Experiments are recorded and quoted showing that many, if not all, crystals separated from solutions contain included mother-liquor.

(*b*) The experiments show also that before the mother-liquor can be eliminated by pulverization the adsorption of water from a moist atmosphere begins to augment the weight of the substance.

(*c*) It is pointed out that this adsorption cannot be wholly overcome in the case of hydrated salts without a loss of water of crystallization also. Hence hydrated salts cannot be accurately weighed according to any usual procedure.

(*d*) In the case of anhydrous salts the elimination of adsorption is easy, but in order to remove included solvent the cell walls enclosing it must be disintegrated.

(*e*) Mechanical, thermal and chemical methods of such disintegration are classified and applied to the preparation of pure materials.

(*f*) It is pointed out that other impurities besides the solvent will usually be enclosed in the cells, and that these other impurities must never be forgotten in subsequent processes of purification.

(*g*) Finally, it is suggested that these enclosed impurities might be used more frequently than they are as a clue to the manner of growth of natural minerals, and hence to the mechanism of geophysical processes.

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A RÉSUMÉ OF THE COMPOSITION AND OCCURRENCE OF PETROLEUM.

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I have said and written so much about petroleum during the last fifteen years, it may seem that I have reached the limit of interest and about exhausted the subject. Twenty years ago when I first went to Cleveland I began the study of petroleum, and have since devoted a considerable portion of my time to the examination of the constituents of petroleum from many different fields. But instead of exhausting the subject it is evident that only a beginning has been made, and the foundation for what is probably the most difficult and intricate parts of this interesting field of research.

The series of hydrocarbons which form the portions of petroleum distilling below 350° *in vacuo*, corresponding to 475° atmospheric pressure, are now well understood, and the members of the various

[1] The subject matter of this paper is based on the results of work carried on in the chemical laboratory of Case School of Applied Science, with aid of grants by the American Academy of Arts and Sciences from the C. M. Warren fund for chemical research.